

# Design of High-Performance, High-Energy Cathode Materials

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es052

# Overview

## Timeline

- Project start date: 10/1/2015
- Project end date: 9/30/2018
- Percent complete: 55%

## Budget

- Total project funding
  - DOE share: 100%
  - Contractor share: N/A
- Funding received in FY 2016:
- \$625k
- Funding for FY 2017: \$625

## Barriers

- Barriers addressed
  - Energy Density
  - Cost
  - Cycle Life

## Partners

- Interactions/collaborations
  - LBNL, BNL, SSRN, UCB, UCSD, NREL
- Project lead: LBNL

# Relevance

- To reach energy density goals, practical capacities of NMCs need to be increased.
- This is probably the fastest route to increasing energy densities. However...
  - This will require cycling to higher potentials vs.  $\text{Li}^+/\text{Li}$
  - e.g., to reach or exceed 250 Wh/kg in a full cell, a Ni-rich NMC (622 or 811) should be cycled to 4.35V (instead of 4.2V). For 622, an advanced anode is also required (e.g., Si-C).
- We need to understand what limits the high voltage cycling behavior of NMCs.
- Some strategies (Ti-substitution, ALD coatings) appear to improve high voltage cycling behavior-understanding these effects will allow us to design better cathode materials.

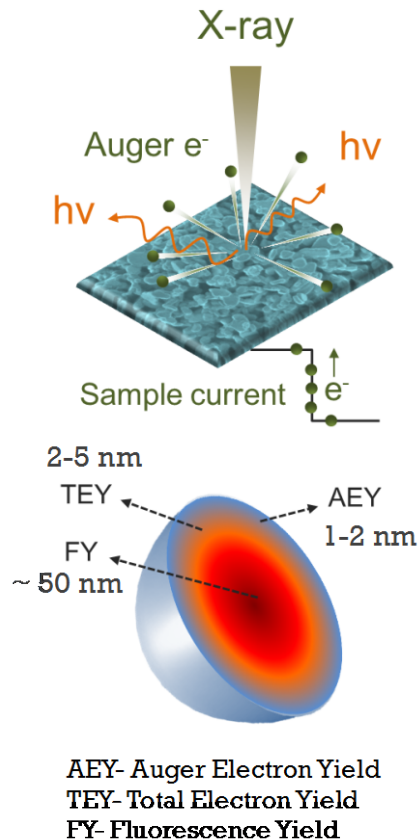
# Objectives

- To develop high energy, high performance cathode materials, with an emphasis on designing NMCs for better high voltage performance.
- First, experiments are carried out to understand high voltage behavior of NMCs made by conventional and novel synthetic procedures.
- Results are used to guide the design of better-performing materials (e.g., metal-segregated NMCs that are Ni-poor on particle surfaces).

# Milestones-FY17 and FY18

Milestone	Date	Status
Synthesize baseline NMC-523 and 622 and Ti-substituted variants	12/31/16	Completed. Decision made to emphasize NMC-622 this year, rather than NMC-523.
Complete surface characterization of pristine materials by synchrotron XAS and XPS	3/31/17	Completed for NMC-622.
Complete soft XAS experiments of electrodes cycled to high potentials.	6/30/17	Completed study of NMC-622. Manuscript in preparation.
Go/no go decision on core-shell composites made by spray pyrolysis	9/30/17	No go decision made. Metal segregation occurs naturally in spray-pyrolyzed samples, so that particle surfaces are already Ni-poor. This one-step process is less complicated and more effective than infiltrating hollow particles and refiring to make core-shell composites.
Complete thermal characterization of candidate NMCs by TXM and X-ray Raman	12/31/17	Data collected. Analysis not yet complete.
Synthesize NMC-811 by spray pyrolysis and conventional methods	3/31/18	On track
Complete surface characterization of pristine and cycled NMC-811	6/30/18	In planning stages
Go/no go decision on Ti-substitution of NMC-811	9/30/18	Discontinue if solid solutions are not formed or Ti-substitution does not benefit electrochemistry.

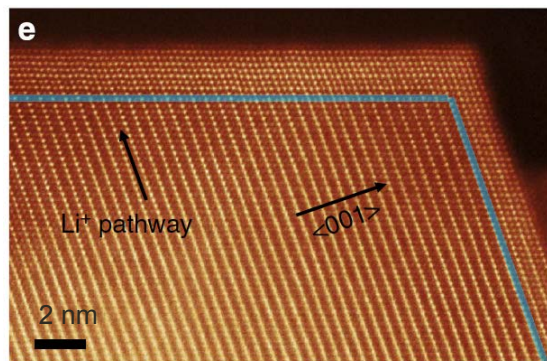
# Approach/Strategy



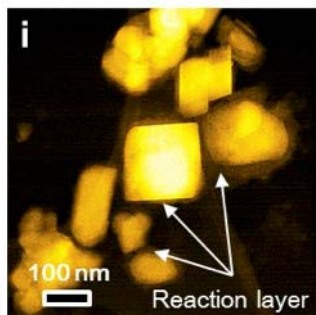
- Use synchrotron techniques (soft XAS, XPS, X-ray Raman, TXM) and microscopy (STEM-EELS) to understand thermal and high voltage cycling behavior of NMCs.
- Develop strategies to improve behavior (e.g., aliovalent Ti-substitution, graded compositions, coatings) and understand their effects.
- Explore alternative synthesis approaches (e.g., spray pyrolysis) that result in less Ni on surfaces of NMCs.

Different modes in  
soft XAS probe  
different sample  
depths

# Background

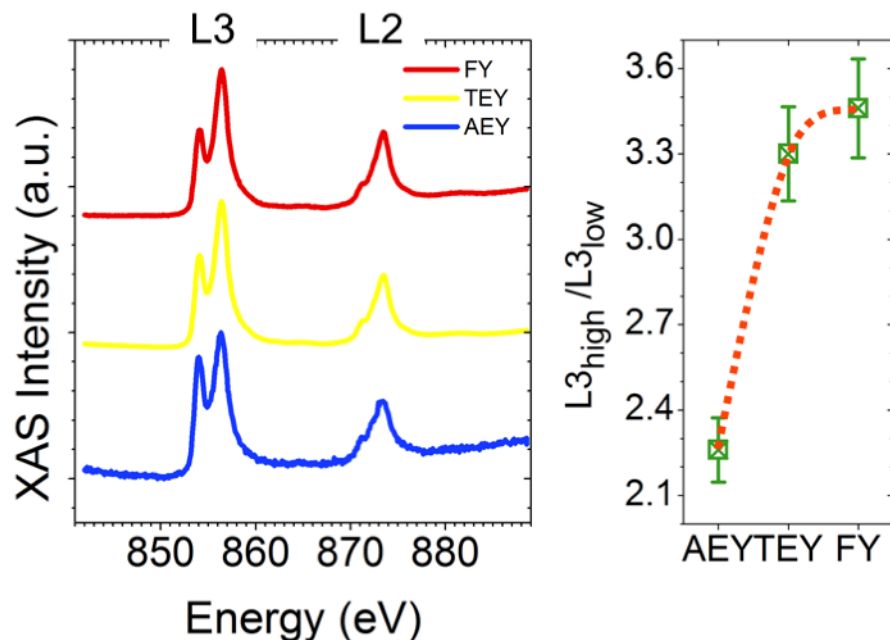


Surface reconstruction to rock salt happens under a variety of conditions

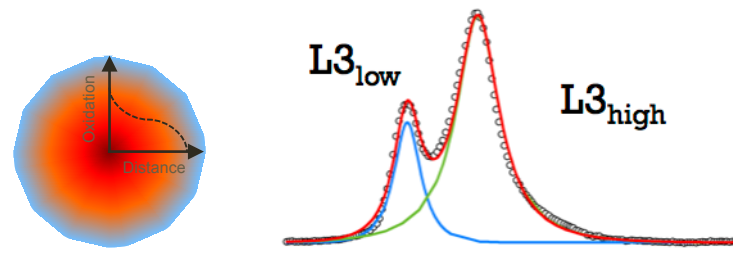


Charging to 4.7V creates a reaction layer (CEI). Not seen after charge to 4.3V

Charged (4.7 V vs Li<sup>+</sup>/Li)

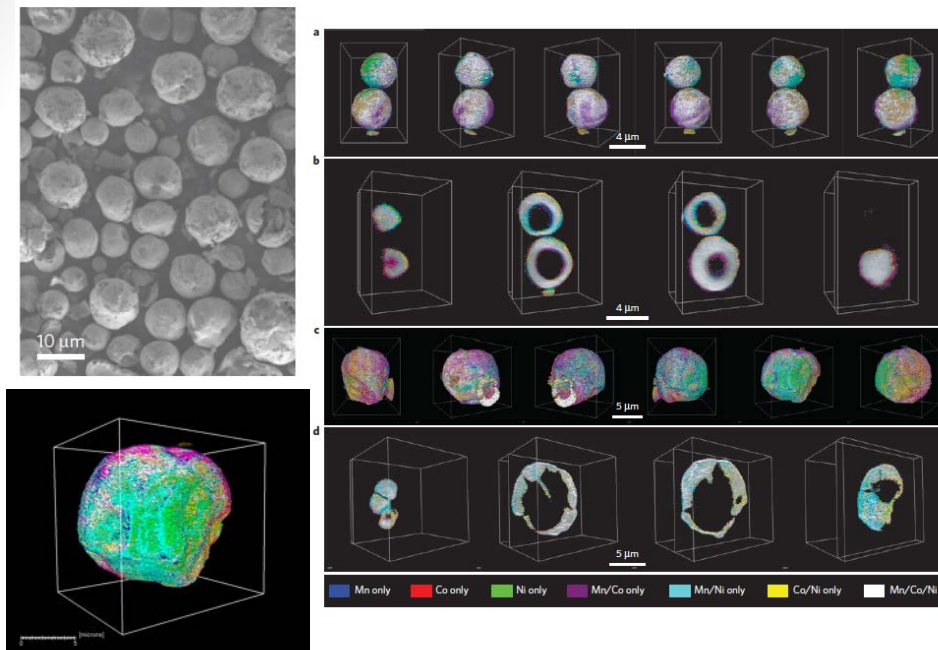


Oxidation state gradient in charged NMC (metals are reduced on surface)

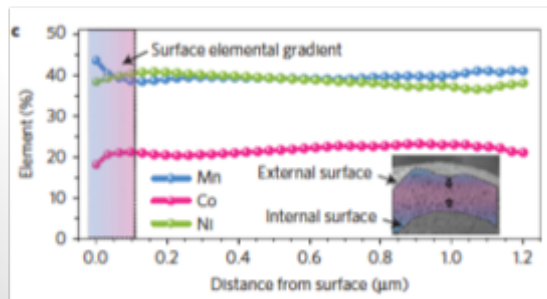


L<sub>3high</sub>/L<sub>3low</sub> related to Ni oxidation states

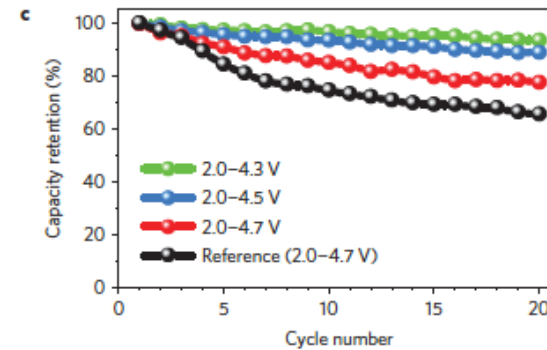
# Background



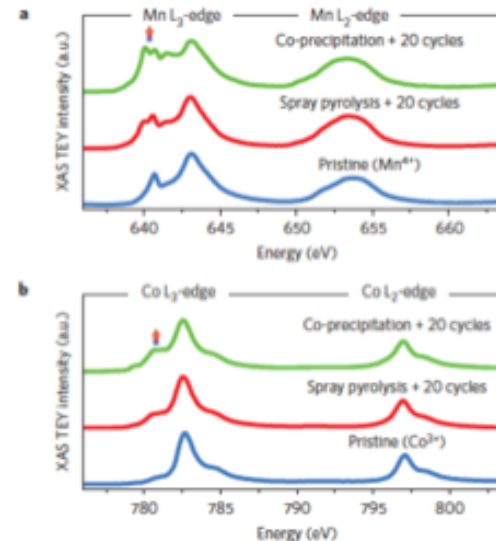
Transmission X-ray Microscopy (TXM, aka nanotomography) shows that there is an elemental composition gradient in an NMC made by spray pyrolysis. There is less Ni on the surfaces of particles than in the bulk.



Quantification of elemental composition gradient



This results in better cycling to 4.7V than for conventional samples



Soft X-ray absorption data

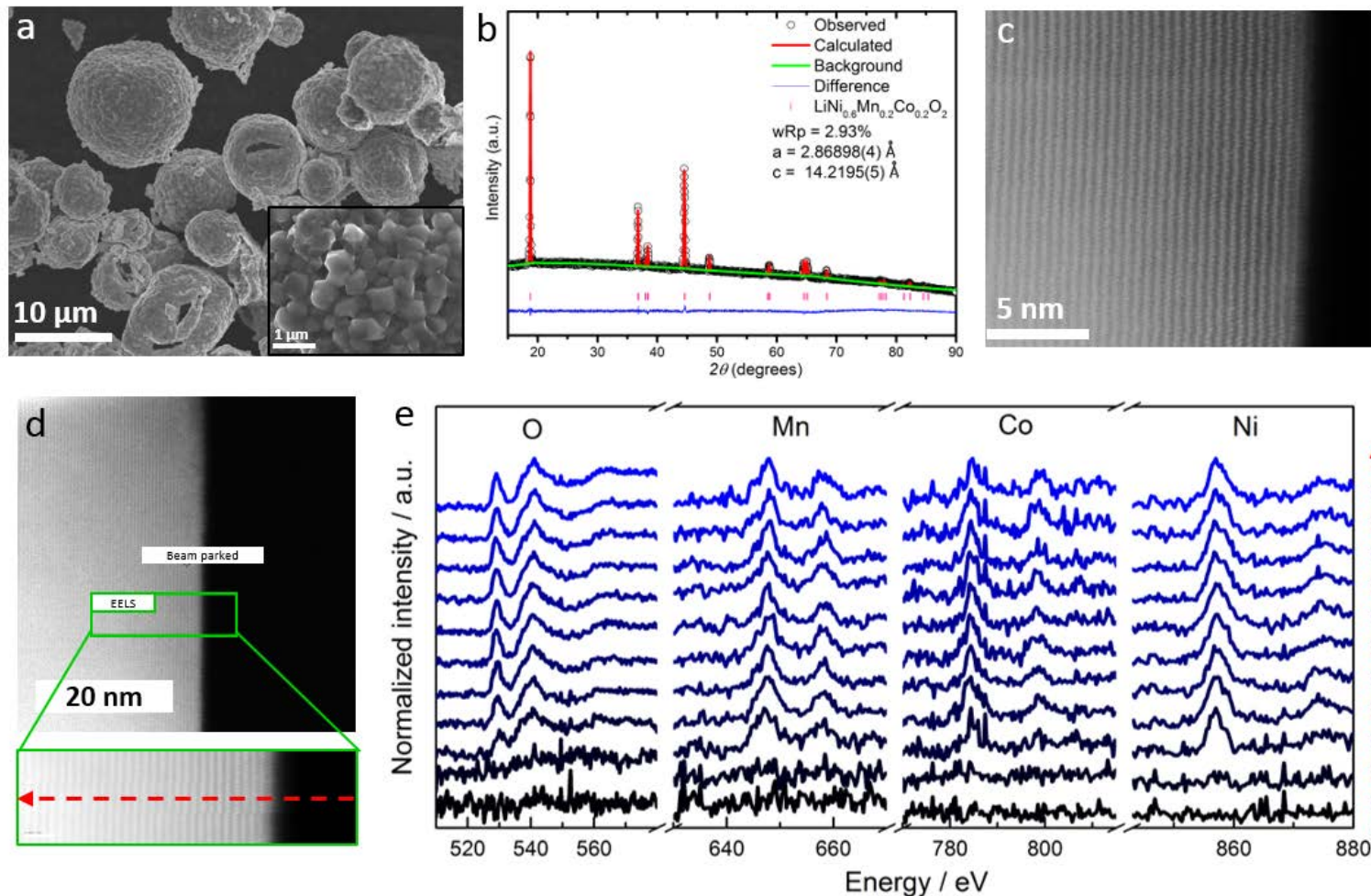
There is less surface reconstruction during cycling of the spray-pyrolyzed sample than the one made by co-precipitation and capacity retention is improved.



NMC-622 studies

# TECHNICAL ACCOMPLISHMENTS AND PROGRESS

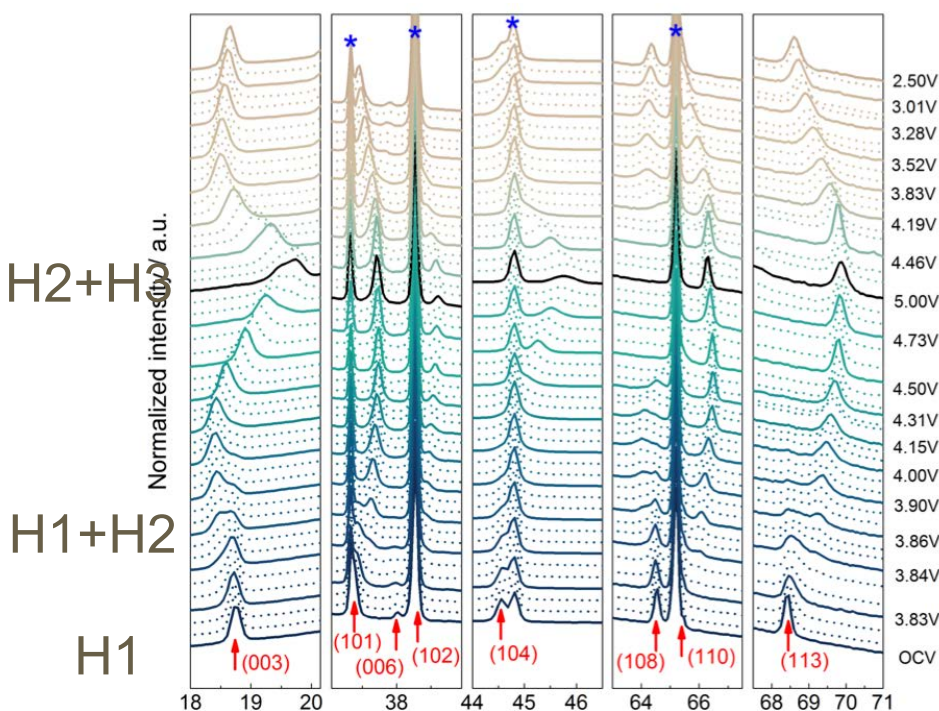
# Pristine NMC-622 Synthesized by Spray Pyrolysis



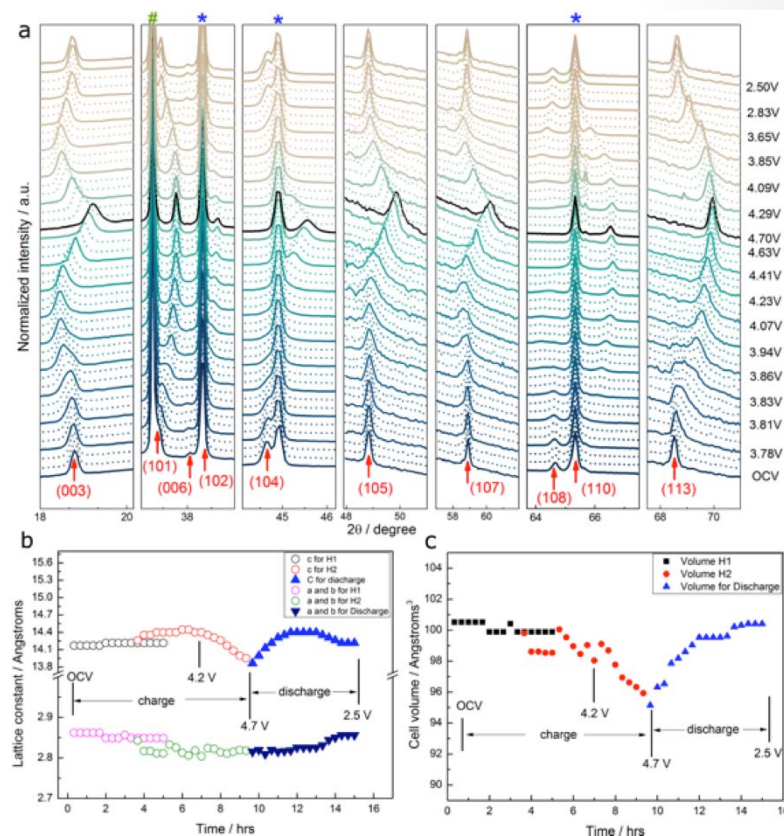
- ❖ Spherical NMC622 particles were prepared by spray pyrolysis
- ❖  $R\text{-}3m$  structure with good crystallinity
- ❖ STEM-EELS data show little change of TM&O oxidation state from surface to bulk

# NMC-622 *in situ* XRD

Cycling to 5V



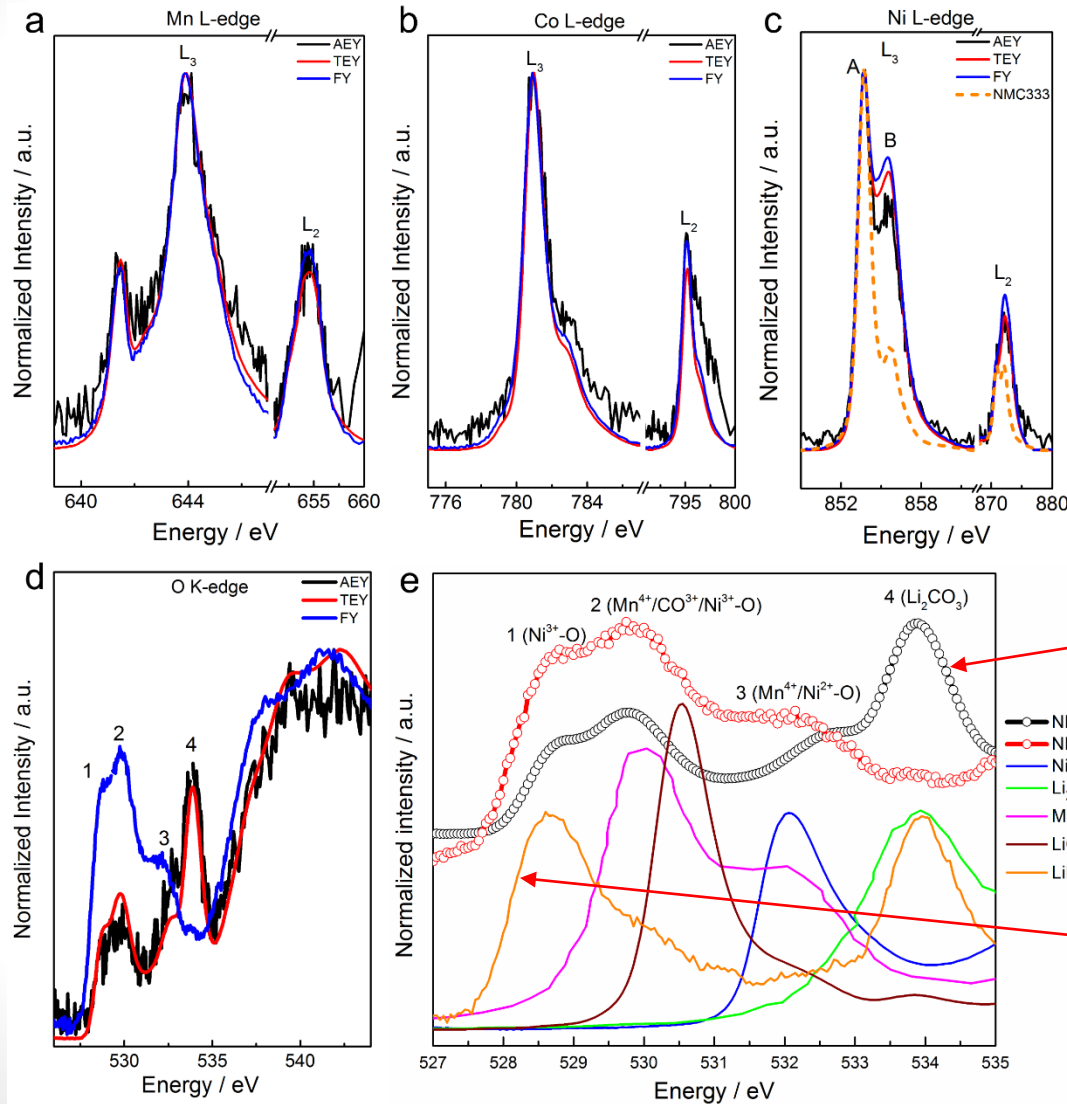
Cycling to 4.7V



Phase behavior similar to  $\text{LiNiO}_2$ , but H3 transition occurs at potentials higher than the practical voltage range typically used in cells

~4% volume change between 2.5-4.7V.  
Excellent reversibility

# Soft XAS (TEY and FY modes) on pristine NMC-622



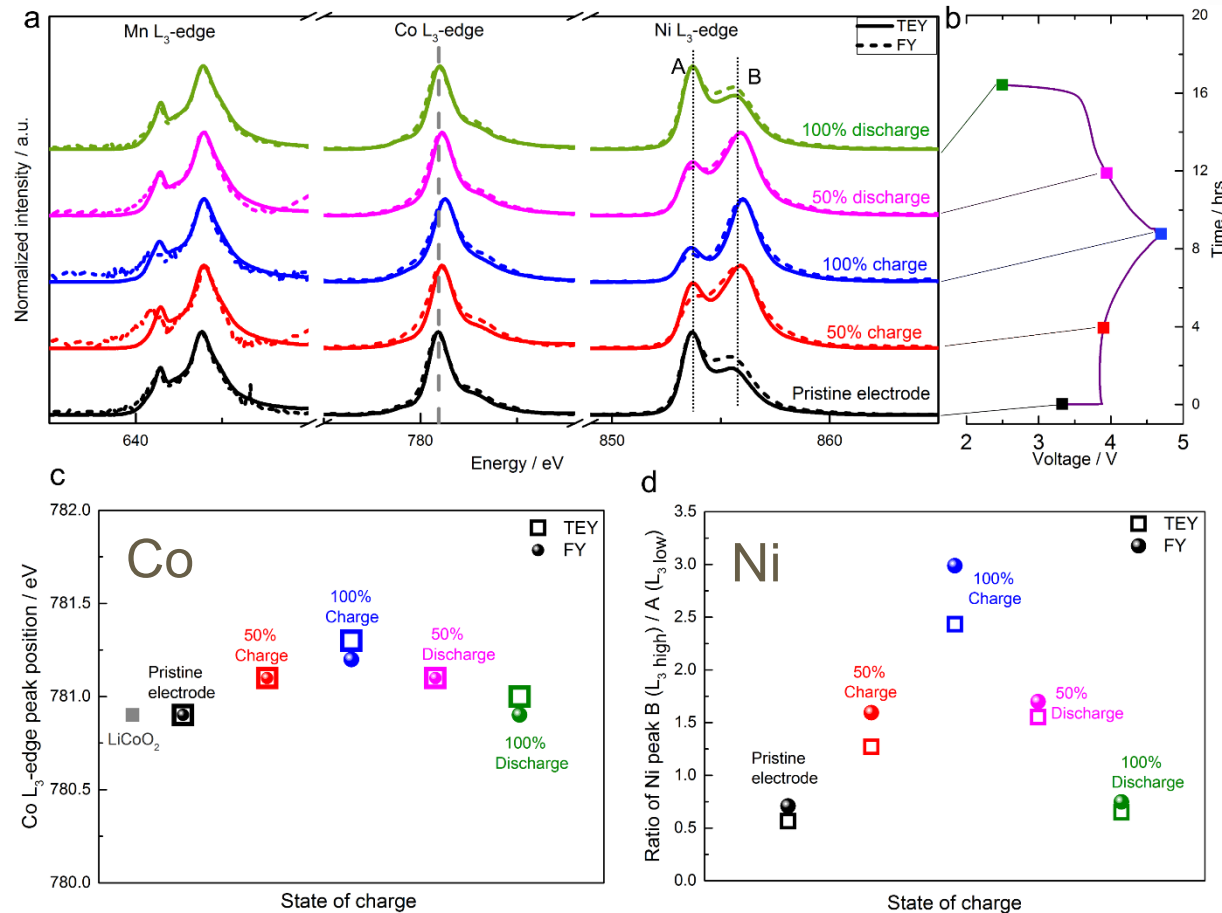
❖ Ni is slightly reduced on particle surfaces compared to bulk, Mn and Co are not. Average Ni oxidation state is much higher than 2+, as expected.

❖  $\text{Li}_2\text{CO}_3$  is formed on surfaces-observed in TEY mode (5 nm), not in FY mode (50 nm).

❖  $\text{Ni}^{3+}$  3d-O2p presents as a shoulder in pristine material.

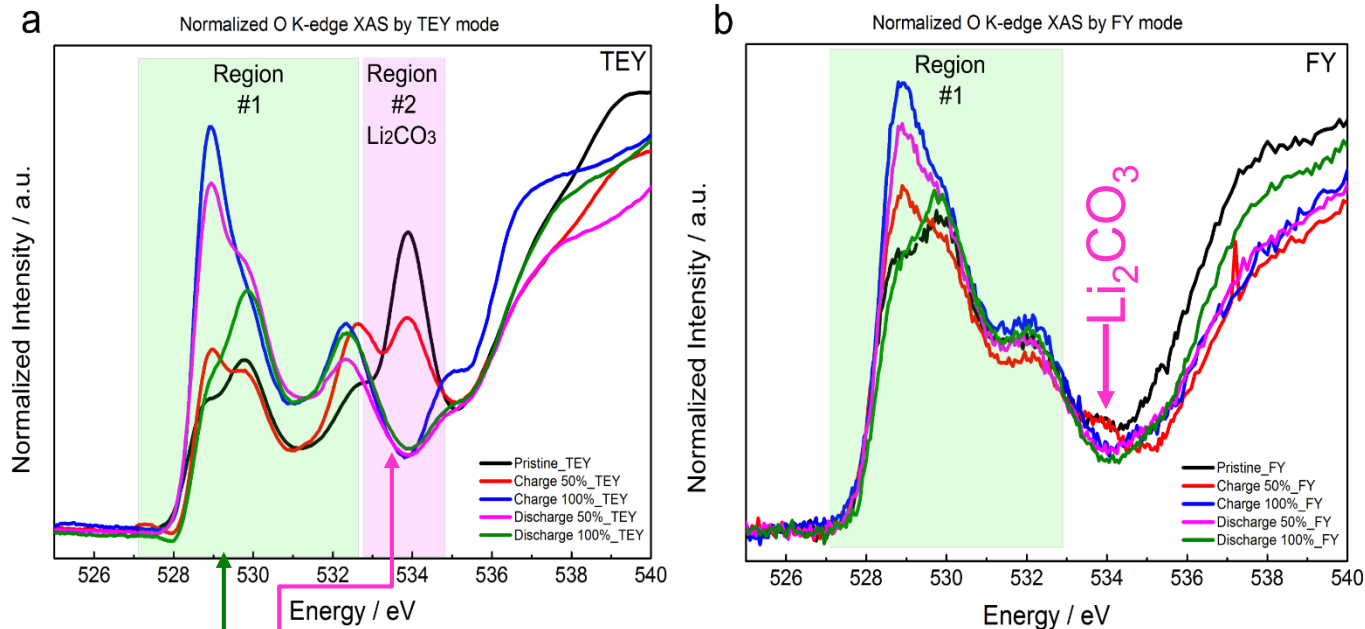


# TM L-edge soft XAS (TEY and FY modes)



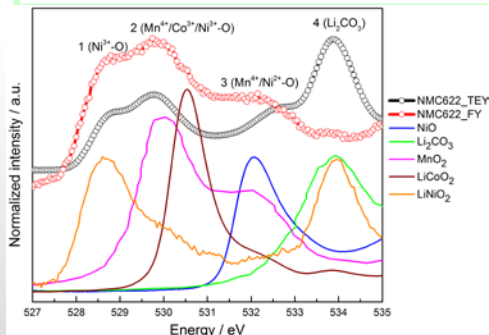
- ❖ Mn remains inactive
- ❖ Some charge compensation with Co, but there is little difference between surface and bulk
- ❖ Ni undergoes significant redox, and surface Ni is less oxidized than in the bulk for all states-of-charge investigated.

# O K-edge soft XAS (TEY and FY modes)



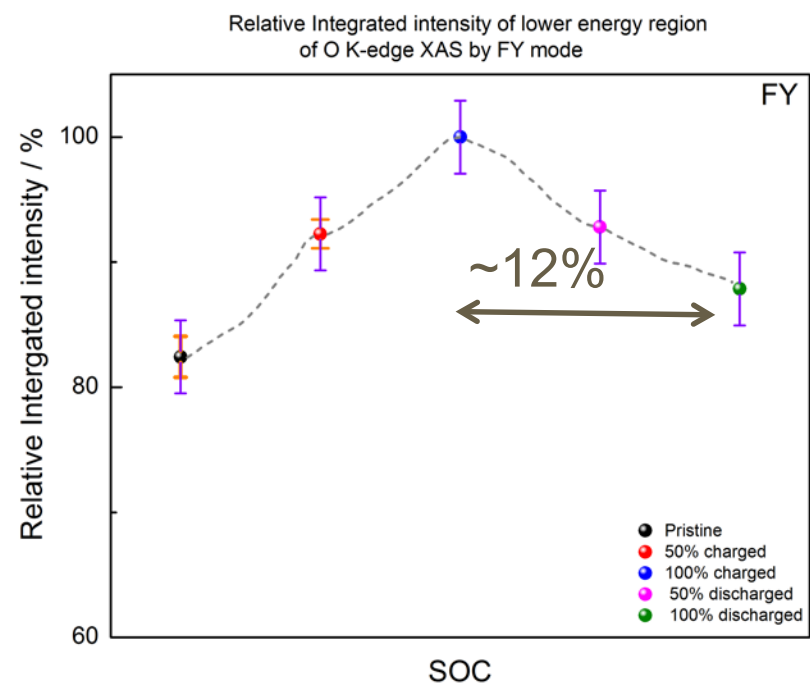
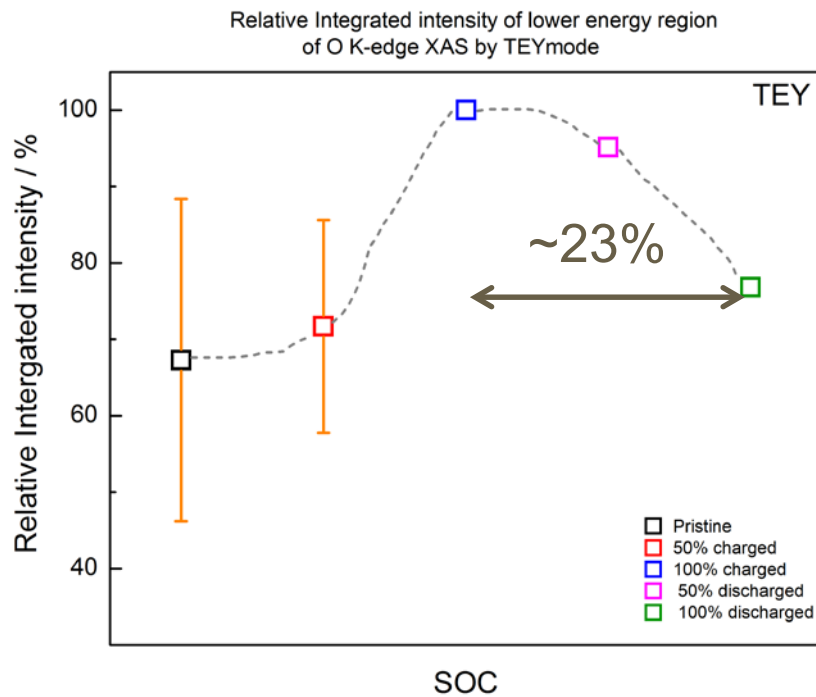
Surface  $\text{Li}_2\text{CO}_3$  disappears after charging.

TM3d-O2p peaks increase in intensity and shift during cycling.



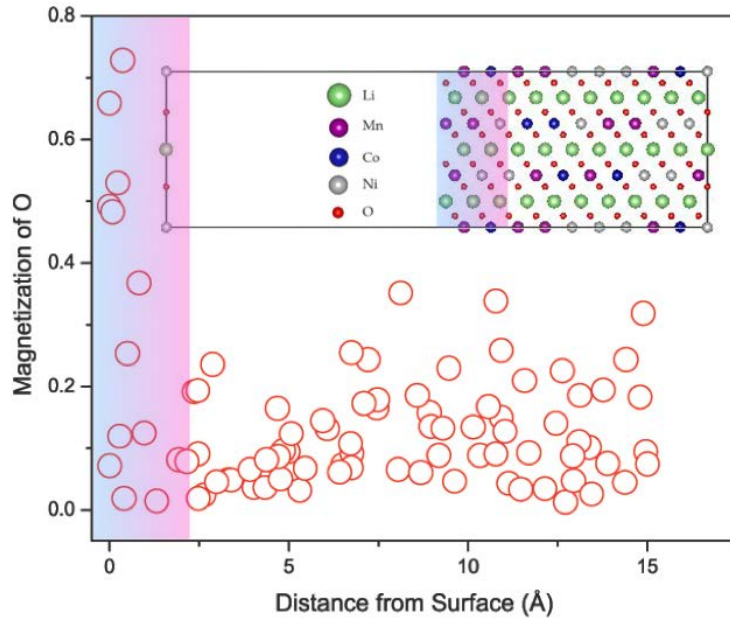
The integrated intensity in region #1 represents the redox activity of the oxygen, since the effective number of holes in the oxygen (through the TM-O interaction) is proportional to this area.

# Semi-quantification of Oxygen Activity Difference for Surface and Bulk



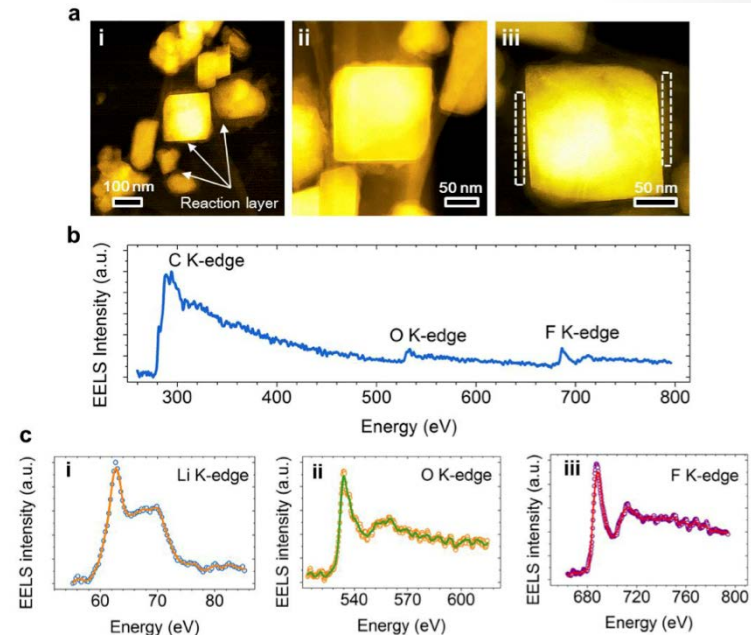
- ❖ Changes are more dramatic in TEY mode than in FY mode=more dynamic changes of hole states on surface.
- ❖ Compare to Ni L-edge results (Ni is more reduced on the surface). These two sets of data taken together indicate that O on the surface is more active than in the bulk.

# Surface Oxygen Activity and Consequences

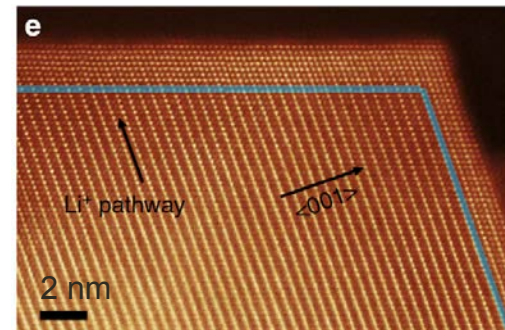


Computational results also indicate that surface oxygen is more reactive than that in the bulk in NMCs. This reactivity explains the strong tendency for surface reconstruction to rock salt to occur under a wide variety of conditions. It may also contribute to reactions at the cathode/electrolyte interface that raise impedance during high voltage cycling.

## CEI formation



## Surface Reconstruction



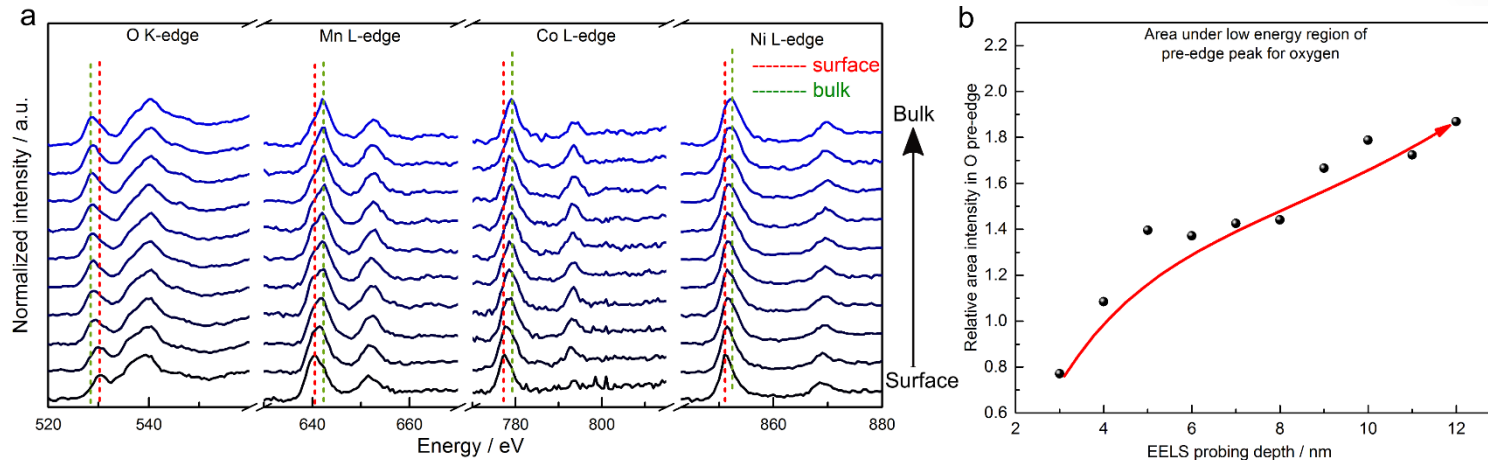
Lin et al. *Nature Commun.* **5**, 3529 (2014)  
and *Energy & Environ. Sci.* **7**, 3077 (2014).



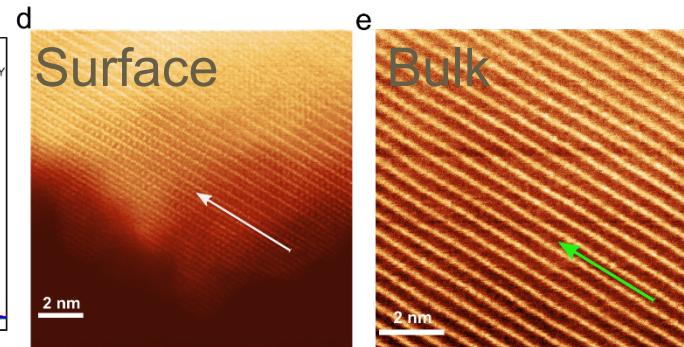
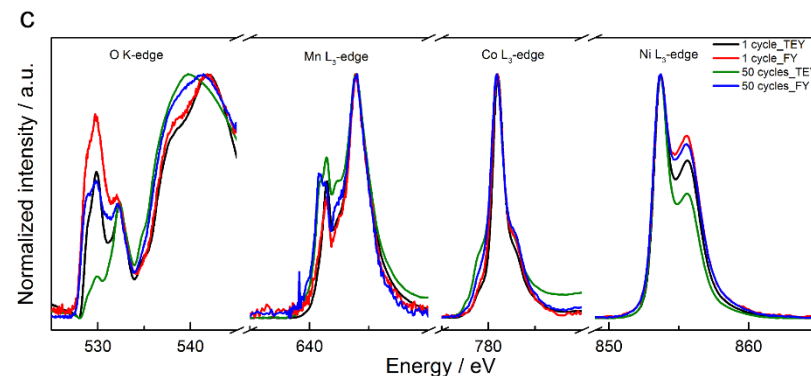
# Crystal and electronic structure changes after 50 cycles

4.7 V – 2.5 V

EELS



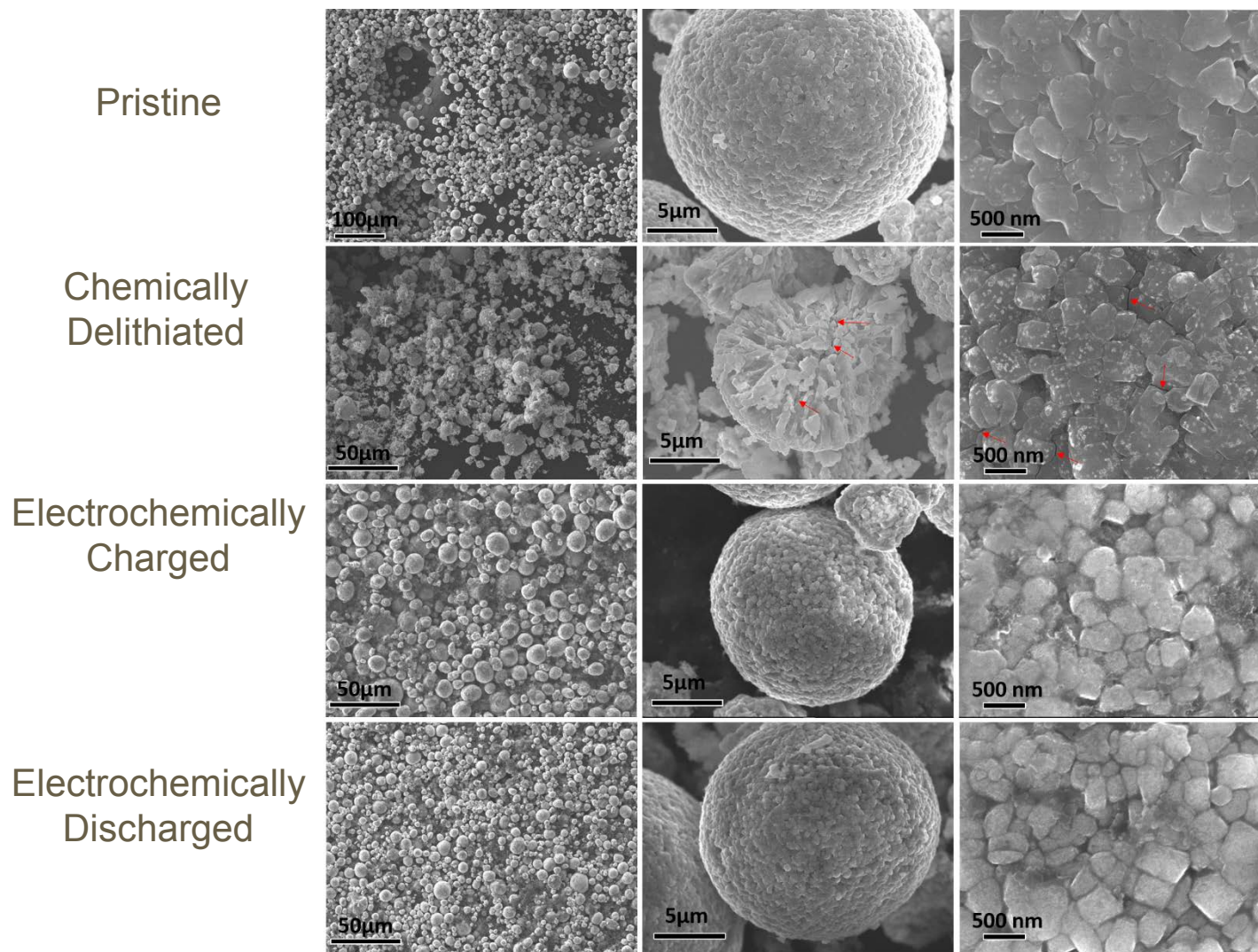
XAS



STEM

- ❖ Both STEM-EELS and soft XAS indicate show metals at surface are reduced compared to the bulk in intensively cycled NMC particles.
- ❖ STEM image shows that at the surface the lithium channels were occupied by transition metals (surface reconstruction).

# Morphology changes during chemical and electrochemical treatment

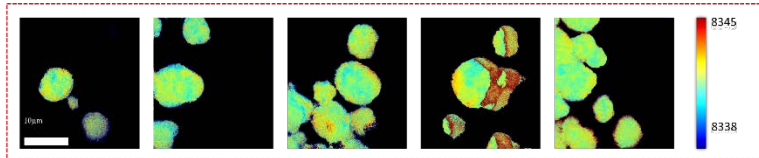


❖ Chemical delithiation leads to disconnection in the secondary particles

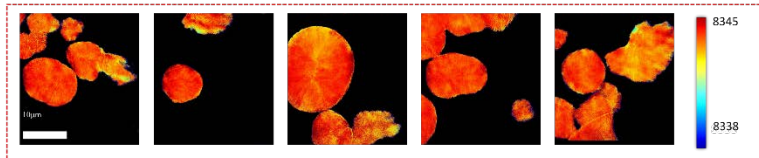
# SOC (Ni K-edge) mapping of NMCs under different conditions

## Ni 2D Transmission X-ray Microscopy (TXM)

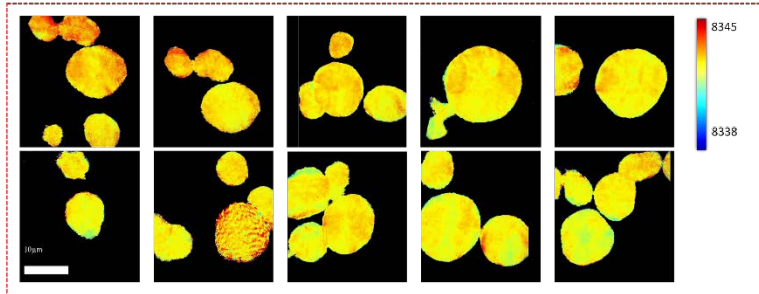
Pristine



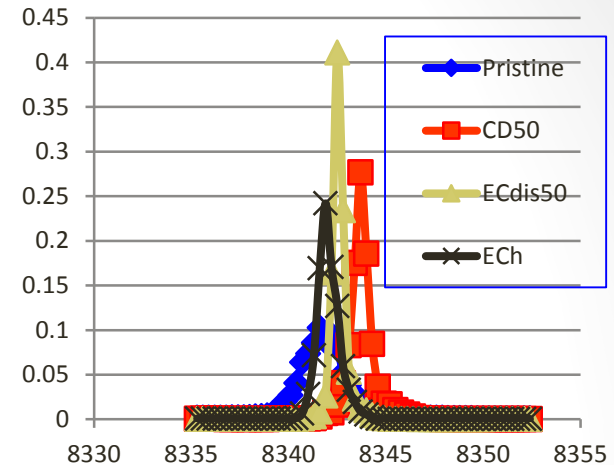
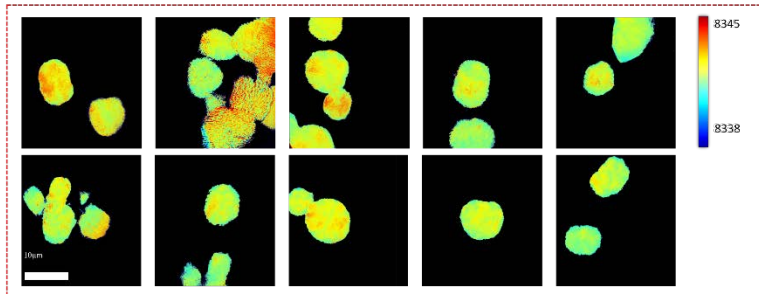
Chemical  
Delithiation  
(50%)



Discharged  
(50%)

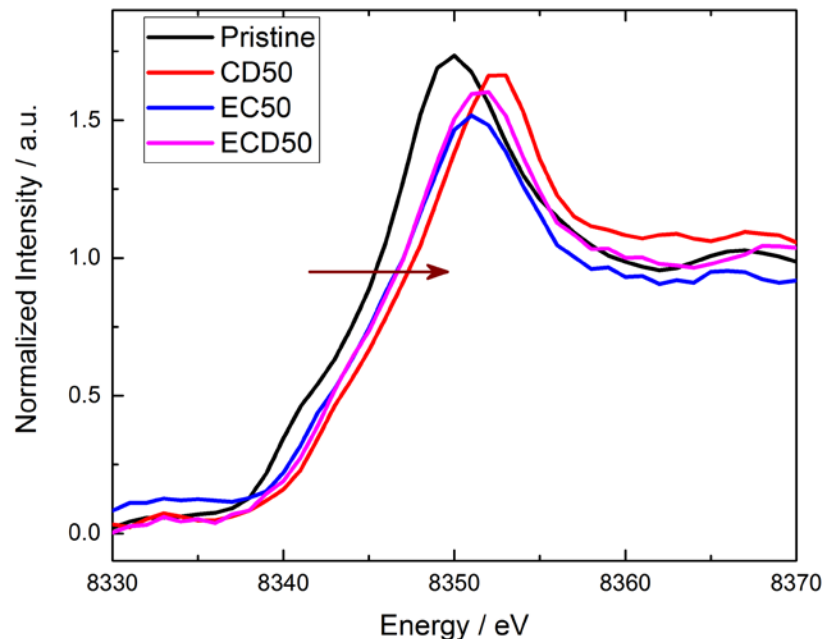
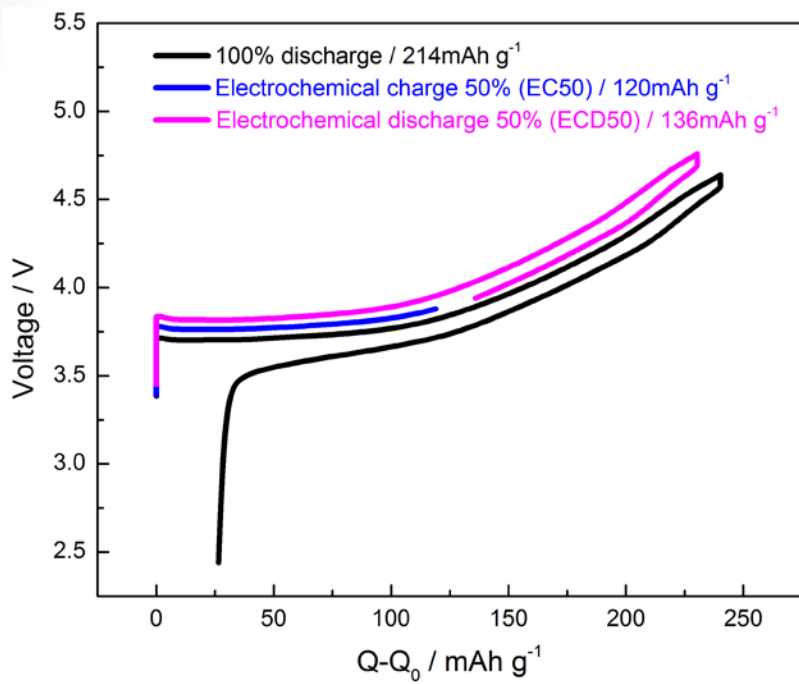


Charged



- ❖ Pristine commercial NMC shows inhomogeneities in Ni valence state distribution within and between secondary particles.
- ❖ Chemical delithiation and electrochemical charge lead to overall oxidation and homogenization of Ni valence state.
- ❖ The absolute Ni valence state (SOC) varies between chemically and electrochemically treated samples

# Origin of variation of Ni K-edge data between electrochemically and chemically treated NMCs

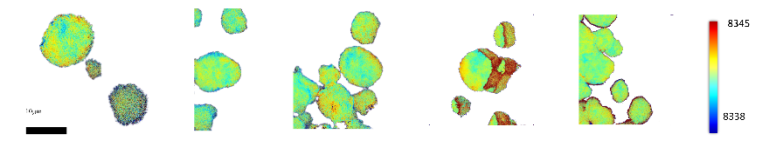


- ❖ Coulometry provides an estimate of expected SOC, but is complicated by cell inefficiencies (e.g., side reactions).
- ❖ XANES data (from ensemble averaged electrodes/large amount of particles) is consistent with the average Ni 2D TXM (multiple particles) mapping data.
- ❖ XANES data is probably a more accurate reflection of SOC than coulometry.

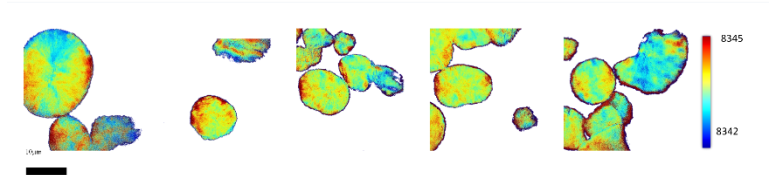


# Homogeneity of NMCs' SOC under different conditions- Different scaling reveals heterogeneity

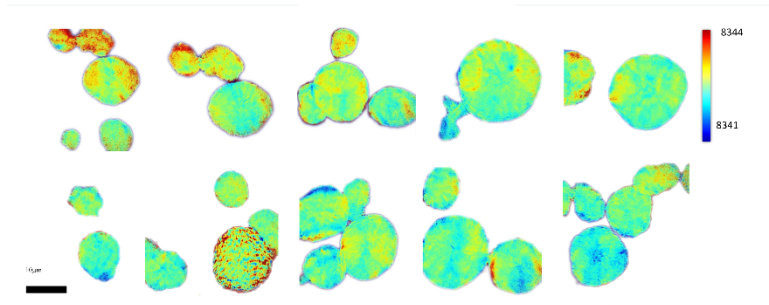
Pristine



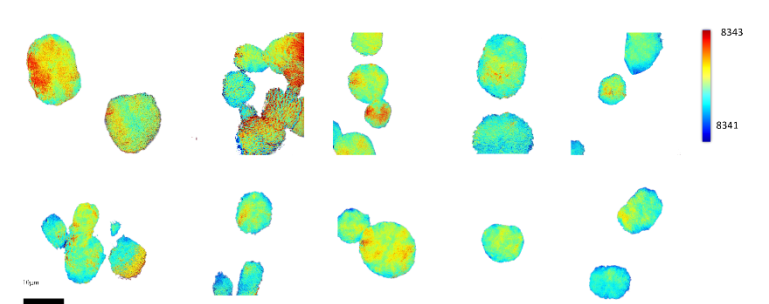
50%  
Chemical  
Delithiation



50% discharged



Charged

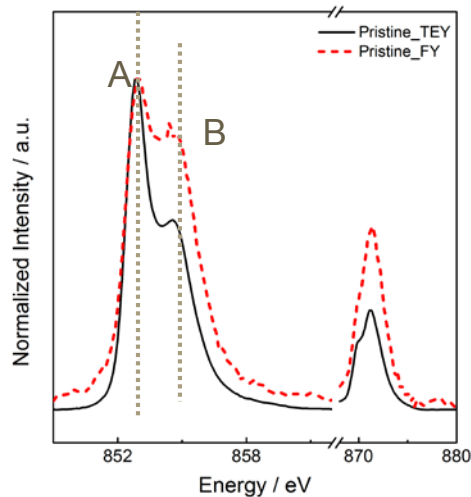


- ❖ Both chemical and electrochemical treatment exhibit heterogeneity of SOC in the secondary particles
- ❖ Electrochemical method---volume-change-induced stress/localized overcharge
- ❖ Chemical delithiation---Mechanical force induced fracture of secondary particles introduces fresh surfaces, which are less oxidized.

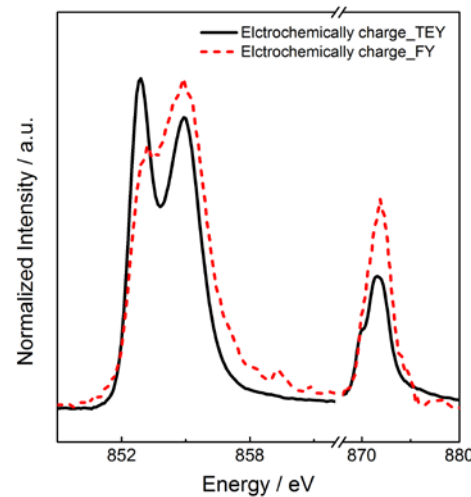
Chemical delithiation and electrochemical treatment show similar levels of inhomogeneity in SOC

# Ni L edge soft XAS (TEY and FY) on chemically and electrochemically treated samples

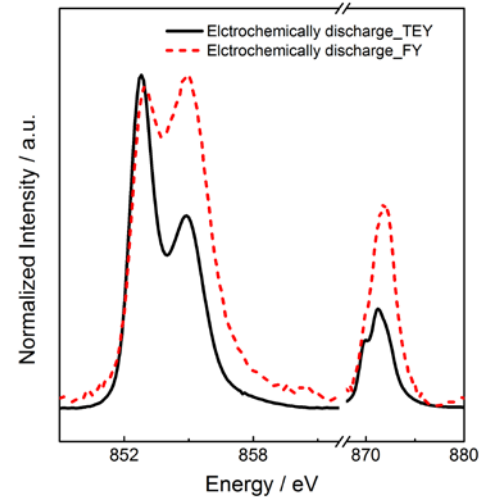
Pristine



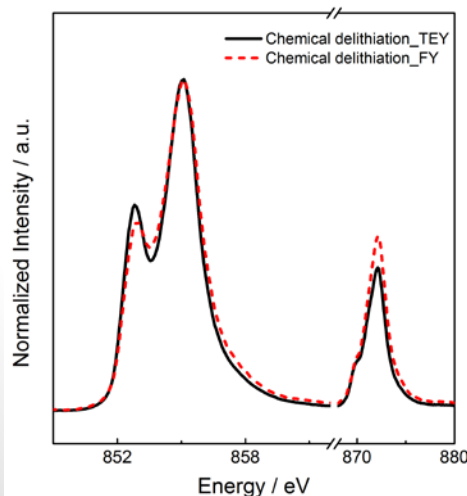
Charged (0.25 cycle)



Discharged (0.75 cycle)



Chemical delithiation



Peak B/A Intensity ratio	Pristine	50% charged	50% discharged	Chemical delithiation 50%
TEY	0.56	0.87	0.57	1.64
FY	0.83	1.28	1.04	1.78
Difference	0.27	0.41	0.47	0.14

- ❖ Electrochemically treated samples show significant surface reduction in comparison with chemically delithiated ones. This suggests exposure to electrolyte plays a role in surface reconstruction.

# Responses to Previous Year Reviewers' Comments

- No comments provided

# Collaboration and Coordination with Other Institutions

Collaborator	Institution	Nature of Collaboration
A. Mehta, D. Nordlund, T.-C. Weng, D. Sokaras, Y. Liu	SSRL	Synchrotron XRD, Raman, imaging, and XAS experiments
Huolin Xin	BNL	STEM-EELS, high resolution TEM
R. Kostecki, W. Tong, B. McCloskey	LBNL	Ni-containing cathodes, Ni-rich NMCs
C. Ban	NREL	ALD and MLD coatings on Ni-rich NMCs
S. Meng	UCSD	Cathodes, synchrotron studies
M. Asta	UCB	Computational studies (shared graduate student Isaac Markus has now obtained his Ph.D.)



# Remaining Challenges and Barriers

- Synchrotron beam time is allocated based on the scores obtained on general user proposals. We have received very high scores on our proposals giving us first priority, but some beam lines are very heavily subscribed and time is limited.
- Data analysis can be time-consuming, particularly for TXM. This means there can be a considerable lag between the experiments and publication/reporting.
- The resolution of the TXM experiment is  $\sim 30$  nm. This limits the types of samples that can be studied (e.g., it's difficult to study nanometric samples).
- For some experiments, we need to use chemically delithiated samples (e.g., TXM). This is why it is important to understand differences between chemically delithiated and electrochemically charged samples.
- Lack of suitable Ti precursors make Ti-substitution in NMCs difficult via the co-precipitation route. There may be more options for spray pyrolysis.
- Multiple strategies will need to be pursued to ensure stable cycling to high potentials, including the use of specially designed electrolytes and ALD coatings.

# Proposed Future Research

- In FY 18, we will concentrate on NMC-811.
- We have already collected ample *in situ* heating TXM data on oxidized NMC-622 and NMC-442 samples to observe effect of Ni content on details of thermal decomposition. We are in the process of analyzing this data, and may also be able to add data on NMC-811 if we receive enough beam time.
- We will study surface and bulk properties of NMC-811 to compare to other compositions we have studied in the past. That way, we can establish a full picture of the effect of Ni content on NMC electrochemical properties.
- We will continue novel synthesis efforts (spray drying, spray pyrolysis) and explore the feasibility of Ti substitution in NMC-811.
- We will continue to collaborate with co-workers at LBNL, C. Ban at NREL, and others to explore approaches towards making Ni-rich NMCs more robust.
- Any proposed future work is subject to change based on funding levels

# Summary

- In pristine NMC-622, Ni has an average valence state higher than 2+, while Mn is tetravalent and cobalt is trivalent. A thin layer of lithium carbonate is present on particle surfaces, which disappears during charge to high voltages.
- In operando XRD on NMC-622 electrodes undergoing charge to 4.7V and discharge to 2.5V show that the bulk structural changes are highly reversible, with an overall volume change of 4% .
- Soft XAS studies indicate that both nickel and cobalt undergo redox during delithiation and lithiation processes, but that Ni in the bulk behaves differently from that on particle surfaces.
- A detailed analysis of the O K-edge spectra indicates the surface oxygen has higher reactivity than the bulk. This is probably a driving force for surface reconstruction and the formation of surface films (CEI).
- Surface reconstruction on NMC-622 is observed after one cycle to 4.7V and becomes more apparent after long cycling.
- Inhomogeneities in states-of-charge are observed in both chemically and electrochemically delithiated samples. For electrochemically cycled materials, volume-change induced stresses may cause inhomogeneities. For chemically delithiated samples, mechanical forces result in particle fracture and the exposure of less oxidized fresh surfaces.
- The surface chemistry of chemically delithiated samples differs significantly from electrochemically delithiated or cycled samples. Soft XAS results suggest that surface reconstruction did not occur on the chemically delithiated samples.